# Evaluation of Synthetic Water-Soluble Metal-Binding Polymers with Ultrafiltration for Selective Concentration of Americium and Plutonium

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Water-soluble metal-binding polymers in combination with ultrafiltration are shown to be an effective method for selectively removing dilute actinide ions from acidic solutions of high ionic strength. The actinide-binding properties of commercially available water-soluble polymers and several polymers which have been reported in the literature were evaluated. The functional groups incorporated in the polymers were pyrrolidone, amine, oxime, and carboxylic, phosphoric, or sulfonic acid. The polymer containing phosphoric acid groups gave the best results with high distribution coefficients and concentration factors for $^{241}$Am(III) and $^{235}$Pu(III)/(IV) at pH 4 to 6 and ionic strengths of 0.1 to 4.

## Introduction

Despite the ability of modern instrumentation to analyze increasingly lower concentrations, elements of regulatory concern are still often at levels near or below the detection limit. Analytical radiochemical counting instrumentation readily allows for measurements of 1 to 10ml volumes, containing 2 disintegrations/minute/ml (2 dpm/ml or 33 Bq/l). Inductively coupled plasma-mass spectrometry (ICP-MS) has a normal working range for routine sample analysis in the parts per billion (ppb) range. Routine counting methods and ICP-MS are unable to directly measure the new United States' Department of Energy (DOE) regulatory level for discharge waters containing alpha-emitting radionuclides of 30 pCi/l (1.1 Bq/l) total alpha or the 0.05 pCi/l (1.8 $10^{-3}$ Bq/l) (~1 $10^{-6}$ ppb for $^{239}$Pu) regulatory level for Pu or Am activity required for surface waters at the Rocky Flats site by the State of Colorado. This inability indicates the need to develop rapid, reliable, and robust analytical techniques for measuring actinide metal ions, particularly americium and plutonium.

The analysis can be further complicated by high concentrations of alkaline or alkaline earth salts and other metal ions in the waste water. High salt concentrations limit the usefulness of preconcentration of samples by evaporation. In such cases selective separation and other preconcentration techniques are

required.[1] Conventional separation and preconcentration techniques (which include extraction chromatography, ion exchange, solvent extraction, co-precipitation, or sorption) have several disadvantages. These methods require interphase transfer of the metal ion and the slower reaction kinetics may require longer contact times. If aqueous solutions are the preferred media for the analysis, additional steps of selective stripping, backextraction, or desorption are required. Other problems arise if the metal ions of interest exist in forms such as colloids, which can require additional treatments. For example, colloidal material can pass through or clog ionexchange resin columns depending on a variety of factors such as bead size, flow rate, and colloid size.

The use of water-soluble metal-binding polymers in combination with ultrafiltration has the potential to be an effective method for selectively removing metal ions from dilute aqueous solutions on both an analytical and a process scale. This method uses water-soluble metalbinding polymers to selectively retain metal ions of interest, while unbound metal ions and small molecular species are removed with the bulk of the aqueous solution as the permeate or filtrate.[2] The advantages of this "polymer filtration" technique are: (1) metal-ion complexation takes place under homogeneous conditions that generally result in enhanced kinetics of binding, (2) colloidal material does not interfere with metal-ion retention, (3) no mixed waste is produced, (4) direct analysis of the concentrate occurs, (5) a reduced number of procedual steps are required, and (6) a variety of analytical instruments can be used to make the final measurements. Polymer filtration has been successfully used for the retention of transition and heavy toxic metal ions, but there have been very few reported studies on the separation and preconcentration of actinide metal ions from waste waters. Bayer and co-workers have reported that the retention at pH 6 of the actinide metalions, uranium [U(VI)], plutonium [Pu(IV)], americium [Am(III)], curium [Cm(III)], and californium [Cf(III)] was achieved with poly(ethylenimine) modified with 8-hydroxyquinoline groups (8HQ).[3,4] They were successful in separating Am(III) and Pu(IV) from U(VI) at pH 4 in the presence of a masking agent, using 8HQ in combination with ultrafiltration. However, there have been no reports in the literature on the selective and quantitative retention of transuranic metal ions by polymer filtration in aqueous solutions having high salt content as found in some process and waste waters. We present here the results of a study using the polymer filtration technique for the recovery of Am and Pu with both commercially available and synthesized watersoluble metal-binding polymers.

**Experimental**

Instruments and equipment used included the following: Fisher Accumet pH meter (model 610A), Orion pH/ISE meter (model 710A), Lab-line orbit environ-shaker, Clay Adams Dynac II centrifuge, Burrell wrist action shaker (model 75),

Mettler balance (model AE240), Supelco Visi- 1 single sample ultrafiltration processor, Supelco HARP syringe-tip hollow fiber membrane (cellulose acetate with 10,000 molecular-weight cutoff, MWCO), Amicon Centricon-10 microconcentrators (10,000 MWCO), Packard liquid scintillation analyzer (model Tri-Carb 2200CA), Beckman scintillation counter (model LS6000), Packard Minaxi auto-gamma counter (Series 5000), and ICP/MS VG-Plasma Quad 2.

*8-Hydroxyquinoline (8HQ) and 4-methyl-8-hydroxyquinoline (Me-8HQ) polymers*

were prepared according to the literature procedure of Yergozhin[5] by reacting chloromethyloxime with a polyamine. The elemental analysis of 8HQ: C = 35.06%, H=8.58%, and N= 19.47%.

*Phosphonic acid polymer (PPO$_3$H$_2$)*

was prepared according to the method of Kobayashi[6,7] from the reaction of formaldehyde and phosphorous acid with a polyamine. The elemental analysis was: C=2.46%, H=5.48%, N=8.7%, and P= 16.88%. FT-IR: (KBr): 3433 cm$^{-1}$ (N-H), 2843, 2354 cm$^{-1}$ (P-OH), and 1058 cm$^{-1}$ (P=0).

*Radioisotope stock solutions*

[241]Am and [238]Pu were obtained from Los Alamos radioanalytical supplies. A [238]Pu(IV) spiking solution was prepared from 5 ml of the 238Pu stock solution, which was placed in a glass vial with 0.2 ml of 1 N hydroxylamine hydrochloride and heated (80 •C) for 10 minutes. The solution was cooled and 0.2 ml of 2M sodium nitrite was added to complete the oxidation state adjustment. The t52Eu(III) was obtained from the National Institute of Standards and Technology (NIST). The 5 ml of solution were concentrated by heating to 3 ml. After spiking, all initial samples were at the tracer level of 8,000 to 100,000 counts/minute/ml (cpm/ml).

*Survey of commercially available polymers, 8HQ and Me-8HQ*

Commercially available functionalized polymers were evaluated in dilute nitric acid for their metal-ion retaining capability. Initial filtration surveys used the Supelco single UF fiber system. The HFM filter was prewetted (3 ml of 1: 1 absolute methanol (Baker): deionized (DI) water) and rinsed with DI water. The polymer solutions were prepared with DI water and polymer concentrations ranged from 0.03 to 0.1 wt/vol. %. The pH values, 2 and 6, were obtained with dilute HNO$_3$ or NaOH (Baker). The polymer solutions were spiked with aqueous acidic [241]Am(III) and shaken or stirred for 30 min. The samples were added to the HARP reservoir and passed through the HFM filter. The actinide content of the

retentate was determined by counting equal volume samples of the starting material and filtrate (permeate), using gamma spectroscopy and calculating the percent metal retained.

*Binding studies of PPO3H2, varying pH, ionic strength and polymer concentration*

These studies used $PPO_3H_2$ with the Amicon Centricon-10 (C-10) filter unit. A stock solution of $PPO_3H_2$ (0.1%w/v) was prepared with DI water then prefiltered (Nalgene, 0.2,u) to remove any colloidal material. Various concentrations of $PPO_3H_2$ (0.001, 0.01, 0.05, 0.1, 0.6%w/v) and $NaNO_3$ (0.1 and 4.0M) were used at pH ranges of 2 through 6. The working solutions were spiked with $^{238}Pu(IV)$ or $^{241}Am(III)$ and titrated with aqueous NaOH and dilute $HNO_3$ to the desired pH values.

The C-10 unit is comprised of two halves, a retentate (top) and permeate (bottom) portion, with the membrane filter incorporated in the retentate half. Initial weights of the top (retentate) and bottom (permeate) units were obtained. Samples were placed in the top half of the C-10 unit and centrifuged at 2200 rpm for 25 min until approximately 1 ml remained as the retentate and 1 ml filtered as the permeate. Final weights were recorded for each unit. The solutions and their accompanying half units were placed into separate liquid scintillation vials and measured using alpha spectroscopy (Beckman). Measuring the complete units (the two halves) with the sample gave 100% accountability because no samples were transferred, thus, no loss of activity occurred from adhesion to the sides of the transfer apparatus. Quenching studies showed Optifluor AF had very low quench values in the presence of the water-soluble polymer, nitrate salts, and the C-10 filter unit. Blanks containing only DI water or 0.1M $NaNO_3$ spiked with $^{238}Pu(IV)$ or $^{241}Am(III)$, titrated to pH 2 and pH 5 were performed to determine metal retention in the absence of polymer.

The adsorption or binding ability of the polymer for metal ions is expressed as the distribution coefficient *(D),* which is defined as: [total bound metal/total free metal] x [phase ratio]. The phase ratio is the initial sample volume (ml)/initial polymer weight (g) used in the experiment. Total bound metal = retentate activity (cpm/g) - unbound activity (cpm/g); and the total unbound metal = permeate activity (cpm/g) + unbound activity (cpm/g); unbound activity = permeate activity (cpm/g) x retentate mass/permeate mass. This formula is similar to the equation that is commonly used to evaluate ion exchange resins in single contact equilibrium binding studies,[8] with a correction made for the unbound actinide that is present in the retentate solution. That correction adds the unbound actinide count in the retentate to the permeate actinide count to obtain total unbound actinide activity. During the ultrafiltration the concentration of the polymer

increased in the retentate as the volume decreased by a factor of two, however we observed little change in the $D$ value as a function of the permeate volume change for tracer levels of metal ions. Filtration of half of the material was therefore chosen as the procedure. Since $D$ values are conditional constants, the same filtration conditions were used for all the experiments, thus allowing for comparison of the data and the development of a rapid survey technique.

*Capacity studies of PPO₃H₂*

A capacity study using 35 ppm Eu(III) from $Eu(NO_3)_3 \cdot 6H_2O$ with various concentrations of polymer (0.00, 0.01, and 0.1% w/v), 1.0M $NaNO_3$ at pH 4, and C-10 unit, was performed to determine when available binding sites became saturated. The permeate was analyzed for Eu by ICP-MS.

*Metal-ion competition studies*

The competition for binding sites on the $PPO_3H_2$ with [241]Am(m) and Fe(m) was studied. The working solutions contained various concentrations of $Fe(NO_3)_3$ (100, 500, 1000, 1500, 2000, and 2500 ppm) with 0.1% w/v polymer and 1.0M $NaNO_3$ at pH 4. The solutions were spiked with [241]Am(m) and separated as described above.

**Results and discussion**

Our approach was to investigate commercially available polymers to determine if their use in a polymer filtration system could achieve high recoveries and concentration factors required for treatment of process and waste waters and for low-level analysis. We did a series of blank studies to determine if there was retention

of [241]Am(III) and [238]Pu(IV) by simple ultrafiltration at the tracer level in the absence of polymer. It was observed that [241]Am(III) was not retained by the ultrafiltration membrane in the absence of polymer at pH 2 and 40% was retained at pH 5 when no ionic strength adjuster was present. When 0.1M $NaNO_3$ was present 25% was retained at the higher pH value. For [238]Pu(IV) a larger amount of metal was retained at both pH values, 35% (31% in 1M NaNO3) at pH 2 and 55% (73% in 1M NaNO3) at pH 5. This is not unexpected as [238]Pu(IV) is known to hydrolyze and polymerize at lower pH values than [241]Am(III). One has to consider these results carefully because the condensation of hydrolyzed metal ions can take a long time to reach equilibrium and the presence of the chelating polymer can influence these reactions in a number of ways. The chelating groups on the polymer can suppress polymerization reactions and even redissolve colloids and precipitates. The polymers can also act as flocculating agents to bring colloidal or

precipitated materials together in larger aggregates depending on factors such as the surface charge on the particulates and the polymer at a particular pH.

The commercially available water-soluble polymers tested are listed in Table 1. [241]Am(III) was chosen for this survey as it represents the trivalent actinides which are normally more difficult to bind than the tetravalent actinides [e.g., Pu(IV)] and it showed the least amount of hydrolysis. Polyacrylic acid had the highest binding of the commercially available polymers at 73%. It was surprising to us that the polyvinylphosphate did not have better binding capability given the good results with the phosphoric acid polymer described below. It is possible that this polymer was not stable under the experimental conditions and or had a wide molecular weight distribution which allowed some smaller material to pass through the membrane. The polyethylenimine polymer also had very low binding of 25% with [241]Am(III). This implies that the backbone polymer has little influence on the overall binding of some of the polymers presented below. From Table 1, the observation of higher [241]Am(III) levels in some permeate with polymer present relative to permeates with no polymer present may be explained by the inhibition of aggregation of hydrolyzed metal species by the polymer or by small molecular weight components of the polymer/metal ion complex, which pass through the UF membrane as mentioned above.

**Table 1.** Polymer (0.1% w/v) Survey for [241]Am Retention

| Polymers | Retention at pH 2, % | Retention at pH 6, % |
|---|---|---|
| Polyethylenimine (BASF) | < 2% | 25% |
| Polyvinylphosphateb (Poly Sciences) | 1% | 11% |
| Polyvinylsulfonic acidb (Poly Sciences) | - | 9% |
| Polyvinylpyrrolidone (Aldrich) | - | < 2% |
| Polyacrylic acid (Aldrich) | 14% | 73% |
| Me-8HQ | < 2% | 19% |
| 8HQ | < 2% | 97% |

When none of the commercially available materials proved particularly promising because their 24lAm(III) retention was less than 75%, we synthesized several chelating polymers reported in the literature that contain derivatives of 8-hydroxyquinoline (8HQ and Me-8HQ).[5] Bayer et al. showed that 8HQ readily binds actinides.[3,4] The initial survey of the synthesized polymers are also shown in Table 1. Indeed, at pH 6 the 8HQ showed high binding of [241]Am(III) (97%). It is interesting that a methyl group substituted for a hydrogen adjacent to the ring nitrogen reduced metal binding from 97 to 19%. This indicates that some

selectivity could be built into these metal-binding polymers based on steric effects.

Though the initial results with 8HQ were promising, more extensive ultrafiltration recovery experiments indicated that it was difficult to obtain high actinide accountability in the absence of the water-soluble polymer at the higher pH values of 5 to 7. Experiments performed at pH 6 found $^{241}$Am(III) activity adhered to the surfaces of the ultrafiltration apparatus. Good accountability was obtained when the pH was lowered to 4 in the absence of the polymers. This indicated that a chelating polymer was needed that functioned well in the pH 4 range, otherwise an analytical method using this approach would have difficulty in maintaining high accountability.

It was thought that a multidentate phosphoric acid polymer might function well at pH 4. We choose polyethylenimine reacted with phosphorous acid/ formaldehyde, which gave a polymer functionalized with methylene phosphoric acid groups (PPO$_3$H$_2$).[6,7] The preliminary experiments in acidic DI water indicated that the phosphoric acid could bind $^{241}$Am(III) under the more acidic conditions. For example, when the pH was 3.9 and polymer concentration 0.1% w/v, 99% of the $^{241}$Am was retained. Whereas, 8HQ gave 8.3% retention of $^{241}$Am(III) and 100% accountability at pH 4.0 and 0.05% concentration. Though the polymer concentrations were different, it was obvious that 8HQ was not a strong enough chelating polymer to perform well at lower pH values.

The PPO$_3$H$_2$ was chosen over other experimental polymers for subsequent examination because of its selectivity, ease of synthesis, and ability to bind trivalent actinides at pH 4. Multidentate phosphoric acid chelating groups have high binding constants for trivalent and tetravalent metal-ions such as the actinides. At low pH values, metal ions have to compete with protons for the donor sites on the polymer. Phosphonic acids are ionized even at low pH values relative to carboxylic acids and oximes.

A systematic study of the binding of $^{241}$Am(III) and $^{238}$Pu(IV) verses pH and ionic strength was conducted. The results are reported in Table 2. It can be seen that both $^{238}$Pu(IV) and $^{241}$Am(III) bind well over the pH range 3 to 6 with $^{238}$Pu(IV) having the higher overall $D$ values. Thus, the pH 4 working range for the analytical procedure should be acceptable for both metal ions. An interesting result from this study as shown in Table 2 is that the $D$ values are larger at the higher nitrate concentration. This result can best be seen at the lower pH values where the $D$ values are smaller. The higher ionic strength will effect both the metal-ion binding constant and the physical properties of the polymer.[9] These polymers are polyelectrolytes and it is known that higher ionic strengths can cause polyelectrolytes to "swell," perhaps providing more accessibility to binding sites.[9]

**Table 2.** Binding Study for $^{241}$Am(III) and $^{238}$Pu(IV) with 0.1% w/v PPO3H2 as a Function of pH and Ionic Strength

| pH | Average log D, % retained | | | |
|---|---|---|---|---|
| | At 0.1 M NaNO$_3$ | | At 4M NaNO$_3$ | |
| | $^{241}$Am | $^{238}$Pu | $^{241}$Am | $^{238}$Pu |
| 1 | 2.07 (10.64%) | 3.35 (68.35%) | 4.44 (96.53%) | 4.61 (97.60%) |
| 2 | 3.94 (89.66%) | 4.70 (98.03%) | 4.91 (98.79%) | 4.69 (98.01%) |
| 3 | 4.81 (98.49%) | 4.90 (98.74%) | 5.06 (99.14%) | 5.30 (99.48%) |
| 4 | 4.81 (98.49%) | 5.48 (99.80%) | 4.81 (98.48%) | 4.78 (98.37%) |
| 5 | 4.85 (98.58%) | 5.44 (99.63%) | 4.84 (98.54%) | 4.83 (98.54%) |
| 6 | 4.91 (98.69%) | 6.44 (99.97%) | 5.12 (99.25%) | 5.13 (99.24%) |

It was also noted that at lower polymer concentration PPO$_3$H$_2$ performed better giving higher average log $D$ values than at the higher polymer concentration as shown in Table 3. Again, this could be a property of the polyelectrolytes as they are known to aggregate above their critical micellular concentration.[1]•

**Table 3.** Binding Study of $^{241}$Am(III) with PPO$_3$H$_2$ as a Function of pH and Polymer Concentration

| pH | Avg. log $D$ of $^{241}$Am at 0.1% w/v PPO$_3$H$_2$ | Avg. log $D$ of $^{241}$Am at 0.1% w/v PPO$_3$H$_2$ |
|---|---|---|
| 2 | 3.94 | 4.02 |
| 3 | 4.81 | 5.52 |
| 4 | 4.81 | 6.06 |
| 5 | 4.85 | 6.43 |
| 6 | 4.91 | 6.55 |

Since Fe(III), which can compete with the actinides, is common in waste waters, the effect of the presence of high concentrations of iron on the binding of tracer $^{241}$Am(III) was determined. The polymer solutions were prepared at lower pH values where all the Fe(III) and Am(III) were mixed and soluble. The pH was adjusted to 4 by the addition of dilute NaOH. The solutions were mixed and then centrifuged. The competition of Fe(III) for $^{241}$Am(III) binding sites on the polymer indicated that 1500 ppm Fe(III) was needed before a decrease in the average $D$ of $^{241}$Am occurred. Up to this level no effect was observed on the $D$ value of $^{241}$Am(III). At the highest Fe(III) concentrations (1500 to 3000 ppm) a reddish

precipitate of Fe(OH)$_3$ was observed even though the [241]Am retention decreased substantially. These results indicate that even in the presence of high concentrations of Fe(III) ($\approx 10^4$ to $10^6$ times the concentration of Am), this polymer still had a high binding ability for [241]Am(III). One has to wonder if Fe(OH)3 is acting as a carrier for the [241]Am(III), as Fe(III) is known to start precipitating even at pH 3. If this was the case, then when large amounts of Fe(OH)$_3$ were observed, we might expect to see an increase in the *D* value for [241]Am(III). Instead we observed a decrease in the *D* value. Thus, the Fe(OH)$_3$ does not appear to coprecipitate a substantial amount of the [241]Am(III) under these conditions.

Europium (Eu), a trivalent lanthanide having similar properties to [241]Am(III), was used to determine the capacity of the polymer at the working pH value. Different concentrations of the polymer were treated with a stock solution of Eu(III) maintained at a constant concentration of 35.5 ppm/pH 4 in 1.0 M NaNO$_3$, and the amount of Eu(III) in the permeate determined by ICP-MS analysis. The capacity study showed that at 0.001% w/v polymer (0.1 mg), 25.21 ppm Eu(II) was seen in the retentate, indicating an excess of Eu(III). This indicates a capacity for Eu(III) of 103 mg Eu/mg polymer (0.68 mmol Eu/mg polymer). The capacity appears to decrease at higher concentrations of polymer with the 0.01% w/v solution giving a capacity of 32.9 mg Eu/mg polymer and 0.1% w/v solution giving 3.5 mg Eu/mg polymer. This behavior has been noted by Geckeler et al.[11] and was attributed to aggregation of the polymer at higher concentrations that inhibited accessibility to binding sites.

## Conclusions

We have been able to show that water-soluble metalbinding polymers with ultrafiltration can be used to remove very low-levels of actinides from aqueous streams containing both high and low concentrations of

nitrate salt. The phosphoric acid polymer gave excellent results over the pH range of 4-6. Metal-ion binding increased at higher nitrate concentrations and decreased at higher polymer concentrations. The polymer could compete for actinide binding even in the presence of high iron concentrations. The use of these polymers for preconcentration of actinides from actual process and waste waters for analysis is under development.

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